AUG 2 4 1988

I28.23:9185

RI 9135

Bureau of Mines Report of Investigations/1988

Dimensional Changes of Select Ceramic Materials Exposed to HCl, HNO_3, and H_2SO_4 Acid Environments

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UNITED STATES DEPARTMENT OF THE INTERIOR

COMPLETED ORIGINAL

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UNITED STATES DEPARTMENT OF THE INTERIOR
Donald Paul Hodel, Secretary

BUREAU OF MINES
T S Ary, Director

Library of Congress Cataloging in Publication Data:

Bennett, James P. (James Philip), 1951-

Dimensional changes of select ceramic materials exposed to HCl, HNO_3, and H_2SO_4 acid environments.

(Report of investigations ; 9185)

Bibliography: 9.

Supt. of Docs. no.: I 28.23:9185.

1. Ceramic materials--Testing. 2. Expansion of solids. I. Maginnis, M. A. II. Title. III. Series: Report of investigations (United States. Bureau of Mines) ; 9185.

TN23.U43 [TA430] 622 s [620.1'42] 88-600110

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UNIT OF MEASURE ABBREVIATIONS USED IN THIS REPORT

°C	degree Celsius	pct	percent
g/cm^3	gram per cubic centimeter	psi	pound (force) per square inch
h	hour	psig	pound (force) per square inch, gauge
in	inch	wt pct	weight percent
L	liter	yr	year
oz	ounce		

DIMENSIONAL CHANGES OF SELECT CERAMIC MATERIALS EXPOSED TO HCl, HNO_3, AND H_2SO_4 ACID ENVIRONMENTS

By J. P. Bennett[1] and M. A. Maginnis[1]

ABSTRACT

The Bureau of Mines investigated the dimensional changes of ceramic materials exposed to acid environments to evaluate construction materials for emerging technology in chemical and metallurgical processes. Six commercial ceramic materials (two red shale, two fireclay, one silica, and one silicon carbide (SiC)) were exposed to H_2O, 20 and 30 wt pct HCl, 40 and 60 wt pct HNO_3, and 10 and 50 wt pct H_2SO_4 at temperatures from 50° to 90° C for 300 days. Linear expansions ranged from a low of -0.02 pct for the silica to a high of 0.45 pct for the red shale. A general ranking of the volume expansion of the materials tested, (from high to low), is as follows: high-porosity red shale A and fireclay B >> low-porosity red shale B and fireclay A > silicon carbide and silica. A general ranking (largest to smallest) of the effect of exposure environments is HCl > H_2SO_4, HNO_3 > H_2O.

An autoclave test method was evaluated. Data obtained from 8- to 24-h exposures were compared with data obtained from the 300-day exposures. The relative expansion trends were similar, indicating that this method could be used as an accelerated test.

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INTRODUCTION

New mineral processing techniques being investigated by the Bureau of Mines and others, such as processing at elevated temperatures and pressures, leaching with acids and bases, chloride leaching, and dissolution in fused-salt baths, require the use of construction materials that have good corrosion resistance. One example is the construction material needed to line leaching vessels used in the extraction of alumina from clay using HCl, HNO_3, or H_2SO_4. In the HCl extraction processes studied by the Bureau, acid concentrations range from 1 to 35 pct (1)[2] and temperatures from 50° to 900° C (2).

Industrial equipment designers, fabricators, and material suppliers of acid processing systems frequently base recommendations for construction materials to be used in acid environments upon experience. Suppliers advise that materials be tested in an environment simulating actual conditions of the industrial process. In general, suppliers only report that their material would pass American Society for Testing and Materials (ASTM) C279 (3) specifications, which deal with H_2SO_4.

Previous Bureau investigations into the effect of various acids on ceramic materials (4-8) showed that certain physical property changes occurred, one of which was volume expansion. Inconsistencies in data trends, however, indicated that a closer examination of this phenomenon was warranted. It was necessary to identify a testing technique that would result in accurate and reproducible data.

Long-term studies (up to 20 yr) on the moisture expansion of floor tile (0 to 8.4 pct porosity) were conducted by Slyh and compared with autoclave treatment of samples (9). Twenty to twenty-five percent of the 20-yr expansion occurred in the first month, with 75 to 85 pct occurring in 10 yr. Tile expansion after a 20-yr outdoor atmosphere exposure was the same as an 1-h autoclave treatment at 200 psi and 195° C. Twenty-year expansions ranged from -0.001 pct for low-porosity to a high of 0.057 pct for the high-porosity tile.

Actual expansion that occurs in structural clay under industrial use conditions is normally less than predicted by laboratory studies (10). Ritchie found autoclaved bricks that were restrained (50 psi load) produced 4 to 24 pct less expansion than unrestrained samples. Expansion, as small as 0.02 pct in building brick, has been shown to be destructive (11-14).

Volume expansion, also known as irreversible growth or swelling, causes a dimensional increase in acidproof brick and is generally thought to be similar to moisture expansion observed in structural clay products. Linear expansion of up to 0.35 pct in acidproof brick has been documented (15), but no published technical information or standard test exists to measure expansion or the influence of such factors as temperature, pressure, load, or exposure environment. Expansion of structural units in acid environments is a critical factor in vessel design. Improper design or construction may result in the brick face spalling, the brick lining arching or buckling away from the substrate, the impermeable membrane rupturing or tearing, or the transfer of damaging stress loads into the substrate structure.

This report discusses the results on volume expansion of two red shale, two fireclay, a silica, and a SiC (clay bonded) brick exposed for 300 days to different temperature and acid concentrations of HCl, HNO3, and H2SO4, as well as short-term autoclave tests.

[2]Underlined numbers in parentheses refer to items in the list of references at the end of this report.

TEST EQUIPMENT AND PROCEDURES

Chemical and physical properties of the ceramic materials tested are listed in table 1. Bulk density and percent apparent porosity were determined for each test specimen before exposure, using ASTM test C20-80 (16). The main chemical difference in the red shale and fireclay samples is in their alkali, alkaline earth, and iron oxide contents. Red shale A and fireclay B have high apparent porosity and low-bulk density compared to red shale B and fireclay A.

The selected ceramic materials were exposed to various acid conditions in the test apparatus (fig. 1), which operates at temperatures up to 250° C. Heat was supplied to the 12-L spherical Pyrex[3] glassware reaction vessels by heating mantels. The temperature was controlled by means of a variable power source and monitored in the reactor by a type K thermocouple. A peristaltic pump was used to withdraw, add, or circulate liquid in the system. The bottom of the vessel was filled with 6-mm Pyrex glass beads to provide a level surface for placement of the test samples.

Volume expansion of samples was monitored in 100-day increments over a 300-day time period. The exposure conditions investigated are listed in table 2. Five samples of the high- and low-porosity red shale and fireclay, the silica, and the SiC materials were exposed as groups to a particular acid environment. Samples were completely immersed in the test solution, which was changed every 100 days when the samples were measured. Samples with 1-in diam by 1.5 in high were prepared for length change monitoring by diamond drilling 0.08-in-diam holes in the center of the 1-in-diam surface to a depth of 0.08 in. A bench micrometer with 0.2 in hardened steel ball attachments (fig. 2) was used to measure length changes to 0.0001 in. The 0.2-in steel ball was centered in the 0.08-in hole and the dimensional change was monitored.

[3]Reference to specific products does not imply endorsement by the Bureau of Mines.

TABLE 1. - Chemical and physical properties of commercial ceramic materials

Property	Red shale		Fireclay		SiC	Silica
	A	B	A	B		
Chemical composition, wt pct:						
SiO_2	64.6	63.3	59.4	68.6	9.6	98.4
Al_2O_3	20.6	20.7	31.7	22.9	0.76	0.51
Fe_2O_3	6.4	5.9	2.0	1.9	0.37	0.12
K_2O	3.6	4.6	3.0	1.5	0.046	0.049
TiO_2	1.6	1.6	1.7	1.4	0.11	<0.05
MgO	0.99	1.3	0.35	0.56	0.035	0.056
Na_2O	0.58	0.57	0.27	0.27	0.017	0.53
CaO	0.39	0.05	0.03	0.06	0.22	0.12
BaO	NA	NA	NA	NA	NA	NA
C	NA	NA	NA	NA	NA	NA
S	NA	NA	NA	NA	NA	NA
SiC	NA	NA	NA	NA	87.9	NA
Apparent porosity, pct	10.86	3.26	5.66	11.6	10.89	11.91
Bulk density, g/cm^3	2.39	2.56	2.38	2.26	2.64	1.90
Cold crushing strength, psi	18,800	20,300	9,800	9,700	14,400	4,100

NA Not analyzed.

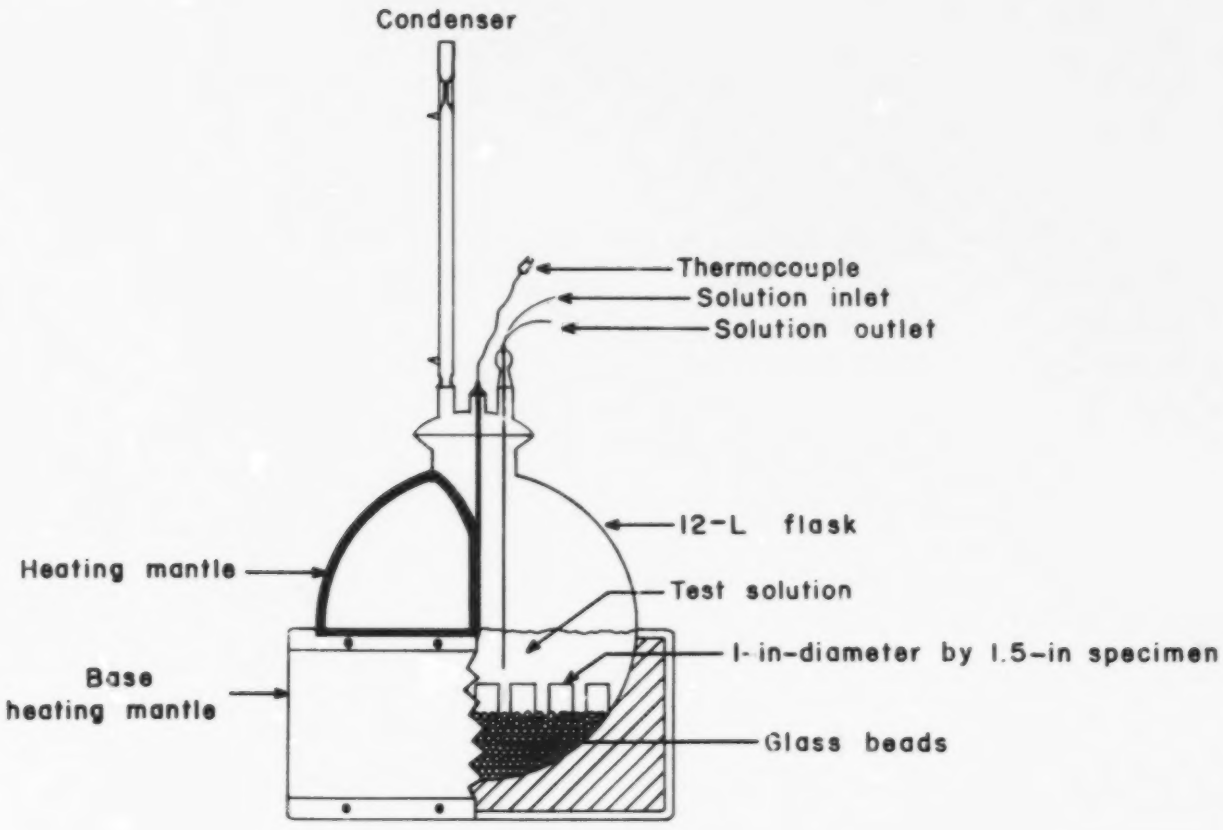

FIGURE 1.–Construction detail of reaction vessel.

Anvil pressure on the 0.2-in balls was adjusted for the lowest setting of 8 oz.

Samples similar to those used in 300-day volume expansion tests were autoclaved in a Teflon fluorocarbon polymer lined autoclave to evaluate autoclaving as an accelerated method of determining linear expansion. Samples were exposed to 20 wt pct HCl, 40 wt pct HNO_3, and 50 wt pct H_2SO_4 at 220 psi for 8 h. Because of smaller expansions observed in water, longer exposure times (24 h) were used to obtain measurable results. The temperature varied between 200° and 230° C for the different acid exposures in order to maintain a 220-psi exposure pressure. Exposure conditions are summarized in table 3. Samples were measured before and after autoclaving using the bench micrometer (fig. 2).

TABLE 2. - Acid conditions evaluated during 300-day exposures, at three temperatures, weight percent

Acid	50° C	70° C	90° C
[1]H_2O.....	NA	NA	100
HCl.....	NA	20, 30	20
HNO_3.....	60	NA	40, 60
H_2SO_4.....	NA	NA	10, 50

NA Not analyzed.
[1]Water data included for comparison.

TABLE 3. - Acid conditions evaluated during autoclaving at 220-psig pressure

Acid	Conc., wt pct	Temperature, °C	Time, h
[1]H_2O.....	100	200	24
HCl.....	20	200	8
HNO_3.....	40	210	8
H_2SO_4.....	50	230	8

[1]Water data included for comparison.

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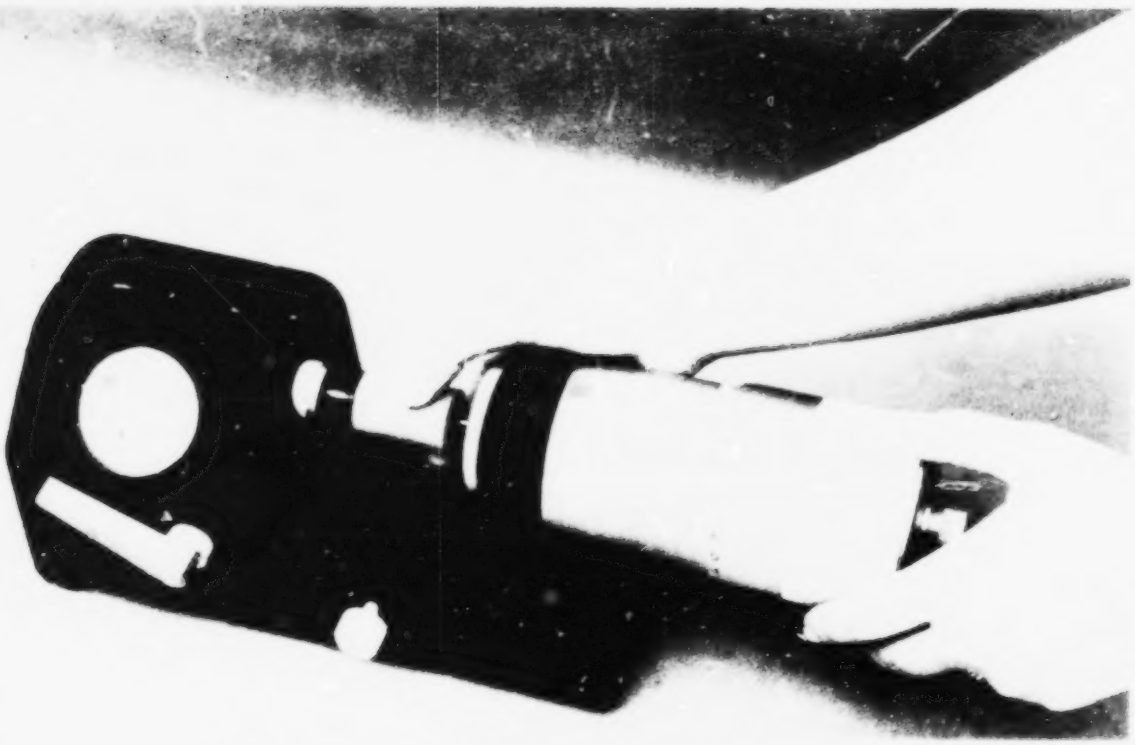

FIGURE 2.–Bench micrometer used to measure length changes.

RESULTS AND DISCUSSION

Linear expansion data of ceramic materials after 100- and 300-day exposure to different acid environments are listed in table 4. Regardless of the exposure time, the high-porosity red shale A and fireclay B materials had statistically significant[4] larger expansions than the corresponding low-porosity red shale B and fireclay A materials. The highest expansion data for each of the individual materials tested occurred in 20 wt pct HCl at 90° C for 300 days, ranging from 0.45 pct for the high-porosity red shale A to 0.08 pct for silica. All 300-day expansions for the silica and SiC materials were less than 0.09 pct.

When the temperature was raised with reference to acid concentration (20 wt pct HCl or 60 wt pct HNO_3), the amount of expansion increased. A continual increase or leveling off of volume expansion with time, over the 300-day period, did not show a clear trend. Typical examples are shown in figure 3, where the slope of the linear expansion curves indicate that dimensional changes may still be increasing (20 wt pct HCl at 90° C) or have leveled off (60 wt pct HNO_3 at 90° C) by the 300th day. A trend for expansion may emerge by testing for longer time periods.

A general ranking of the volume expansion of the materials tested, from high to low, is as follows: high-porosity red shale A and fireclay B >> low-porosity red shale B and fireclay A > SiC and silica. A general ranking (largest to smallest) of the effect of exposure environments is HCl > H_2SO_4 and HNO_3 > H_2O.

[4]Statistically significant changes (Student's t-test) at 95-pct-confidence intervals (17).

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TABLE 4. - Linear expansion of ceramic materials after 100- and 300-day exposures, percent

Exposure condition	Red shale A	Red shale B	Fireclay A	Fireclay B	Silica	SiC
100-day exposure:						
90° C, H_2O	0.050±0.006	0.032±0.005	0.018±0.005	0.049±0.017	[1]0.025±0.022	0.015±0.011
70° C, 20 HCl	.045± .010	.030± .010	.021± .009	.044± .005	[1].028± .031	.020± .007
90° C, 20 HCl	.080± .012	.050± .014	.041± .009	.074± .009	.050± .005	[1].026± .015
70° C, 30 HCl	.041± .001	.032± .005	.025± .010	.037± .005	.032± .005	[1].009± .013
90° C, 40 HNO_3	.064± .018	.034± .001	.018± .005	.055± .008	[1].025± .005	NA
50° C, 60 HNO_3	.016± .005	.007± .001	.009± .005	.016± .005	[1].009± .013	NA
90° C, 60 HNO_3	.057± .005	.039± .010	.030± .004	.050± .010	[1].021± .017	NA
90° C, 10 H_2SO_4	.061± .015	.045± .010	.028± .008	.065± .013	[1].021± .023	[1].015± .013
90° C, 50 H_2SO_4	.048± .001	.034± .009	.028± .001	.058± .006	.027± .008	[1].009± .011
300-day exposure:						
90° C, H_2O	.123± .029	.055± .026	.022± .010	.099± .033	[1].011± .039	[1].002± .048
70° C, 20 HCl	NA	NA	.060± .024	.109± .023	[1]-.022± .054	.069± .020
90° C, 20 HCl	.449± .063	.142± .052	.135± .036	.359± .087	.076± .024	.087± .068
70° C, 30 HCl	NA	NA	.037± .018	.065± .013	.049± .036	.042± .038
90° C, 40 HNO_3	.220± .051	.098± .016	[1].065± .028	.207± .075	.071± .029	NA
50° C, 60 HNO_3	.039± .015	.027± .018	[1].006± .033	.024± .014	[1].030± .022	NA
90° C, 60 HNO_3	.151± .020	.092± .025	.064± .027	.135± .024	[1].039± .043	NA
90° C, 10 H_2SO_4	NA	NA	.050± .032	.184± .049	[1].045± .045	[1].052± .045
90° C, 50 H_2SO_4	NA	NA	.058± .018	.231± .044	[1].018± .028	[1].034± .055

NA Not analyzed.

[1]Not statistically significant; other data are statistically significant changes at 95-pct-confidence level (Student's t-test).

NOTE.--Plus-minus (±) values are at 95-pct-confidence intervals.

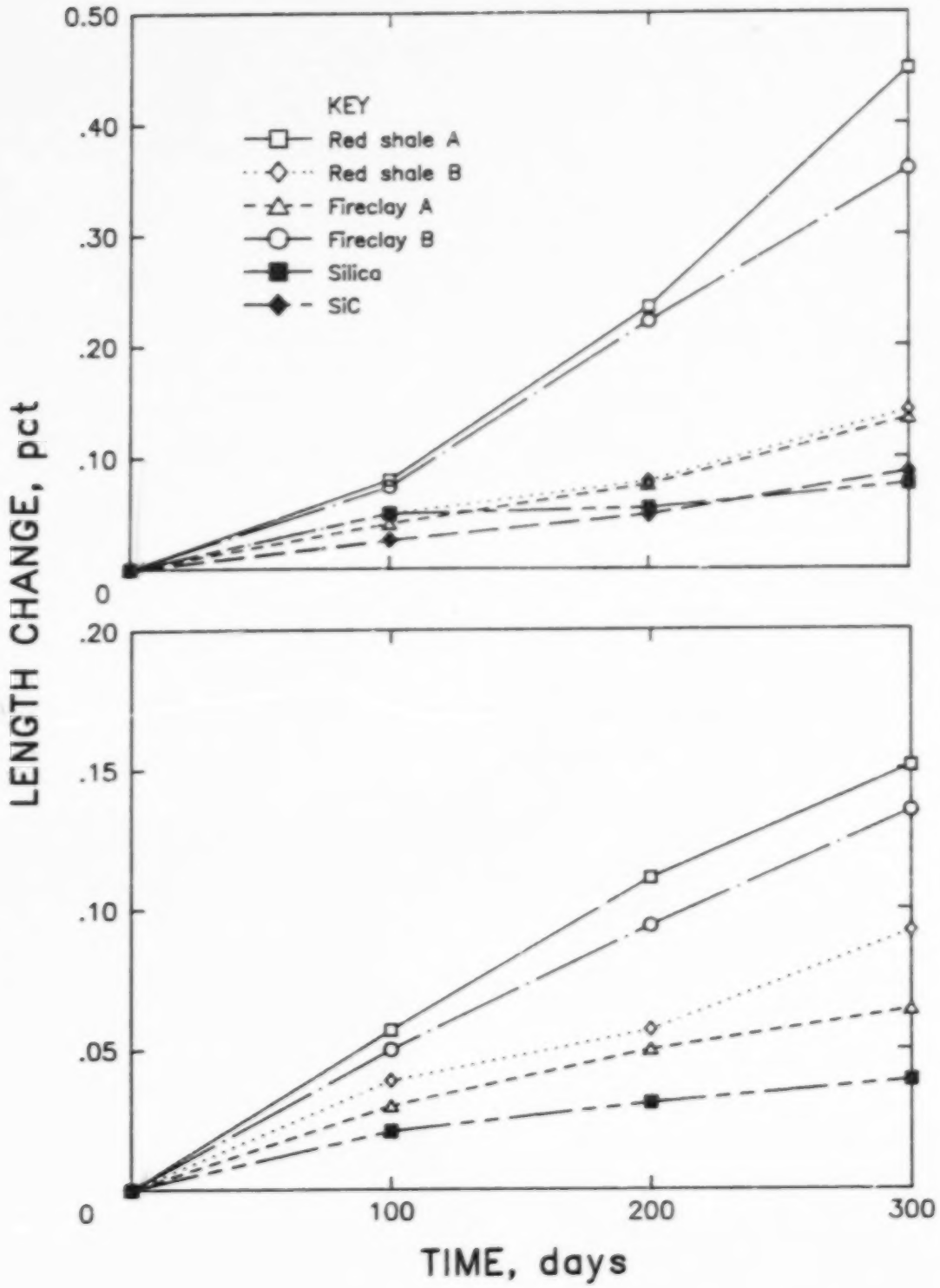

FIGURE 3.–Linear expansion of ceramic materials exposed to 20 wt pct HCl (top) and 60 wt pct HNO_3 (bottom).

The results of accelerated autoclave volume expansion tests in different environments is shown in table 5. Regardless of the exposure condition, the high-porosity red shale A and fireclay B samples had greater expansion than the corresponding low-porosity materials. This same trend was noted for 300-day volume expansion measurements, and is summarized in table 6 for comparison.

Eight hours of autoclave exposure to 50 wt pct H_2SO_4 at 230° C resulted in the most expansion for all the ceramic materials tested. The expansion ranged from 0.094 pct for the high-porosity red shale A to -0.002 pct for silica. The expansion observed in the silica and SiC materials was usually small or negative. Samples autoclaved in water for 24 h had expansions ranging from a high of 0.105 pct for the high-porosity red shale A to a low of -0.029 pct for the silica brick. As mentioned previously, samples were autoclaved for 24 h in water because of the small expansions produced in 8 h. Compared to acid exposures of 8 h, water exposures resulted in much smaller expansions. The relative expansion trends between 300-day atmospheric exposures and autoclaved samples were comparable, suggesting autoclaving of samples as an accelerated method for comparing volume expansion of different ceramic materials exposed to acid environments.

TABLE 5. - Linear expansion of ceramic materials after autoclaving at 220 psig, under four exposure conditions, percent

Ceramic material	H_2O, 200° C 24 h	20 wt pct HCl, 200° C, 8 h	40 wt pct HNO_3, 210° C, 8 h	50 wt pct H_2SO_4, 230° C, 8 h
Red shale A.....	0.105±0.009	0.077±0.023	0.041±0.008	0.094±0.012
Red shale B.....	.049± .004	[1].006± .030	.017± .012	.032± .011
Fireclay A.....	.023± .014	[1].013± .026	[1].008± .017	.061± .017
Fireclay B.....	.103± .010	.054± .022	.024± .012	.088± .013
Silica.....	-.029± .021	[1]-.037± .043	-.019± .016	[1]-.002± .007
SiC.....	.059± .040	-.064± .024	NA	-.065± .018

NA Not analyzed.

[1]Not statistically significant; other data are statistically significant changes 95-pct-confidence level (Student's t-test).

NOTE.--Plus-minus (±) values are at 95-pct confidence intervals.

TABLE 6. - Comparison of 300-day[1] and autoclave[2] dimensional changes of ceramic materials exposed to three different acid environments, percent

Ceramic material	20 wt pct HCl		40 wt pct HNO_3		50 wt pct H_2SO_4	
	300-day	Autoclave	300-day	Autoclave	300-day	Autoclave
Red shale A.....	0.449	0.077	0.220	0.041	NA	0.094
Red shale B.....	.142	.006	.098	.017	NA	.032
Fireclay A.....	.135	.013	.065	.008	0.058	.061
Fireclay B.....	.359	.054	.207	.024	.231	.088
Silica.....	.076	-.037	.071	-.019	.018	-.002
SiC.....	.087	-.064	NA	NA	.034	-.065

NA Not analyzed.

[1]300-day exposure = atmospheric pressure, 90° C.

[2]Autoclave conditions = 8 h at 220 psi, temperature of HCl = 200° C, HNO_3 = 210° C, and H_2SO_4 = 230° C.

CONCLUSIONS

Volume expansion was evaluated on samples of two red shale, two fireclay, one silica, and one silicon carbide ceramic material exposed to water and acid conditions using a long-term and an accelerated test. Results indicated the following:

1. A general ranking of the volume expansion of materials tested at atmospheric pressure, from largest to smallest expansion, is high-porosity red shale A and fireclay B >> low porosity red shale B and fireclay A > SiC and silica.

2. A general ranking of the effect of acid environments on expansion during atmospheric exposure, from largest to smallest, is HCl > H_2SO_4, HNO_3 > H_2O.

3. Increasing the temperature at a given acid concentration resulted in an increase in volume expansion during 300-day atmospheric exposures, while changing acid concentration at a given temperature followed no specific trend.

4. The relative expansion trends between 300-day atmospheric exposures and autoclaved samples were comparable, suggesting autoclaving of samples as an accelerated method for comparing volume expansion of different ceramic materials exposed to acid environments.

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U.S. GOVERNMENT PRINTING OFFICE: 1988 — 547-000/80,067

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